

Gas phase oxygen effect on chain scission and monomer content in bulk poly(methyl methacrylate) degraded by external thermal radiation

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(Received 6 August 1995; accepted 29 September 1995)

The effect of atmospheric oxygen on the thermal decomposition of poly(methyl methacrylate), PMMA, in a slab-like configuration was investigated. Blackbody irradiation of 12 mm thick PMMA slabs on one side was used to simulate the thermal decomposition and gasification of the polymer in a fire environment. Results are reported for chain scission number obtained from molecular weight measurements and for residual monomer content at various levels below the slab surfaces irradiated at 17 and 30 kW/m² in atmospheres containing 0, 10, 21, and 41% oxygen in nitrogen.

The scission number and polydispersity of surface layers, about 0.1 mm thick, were found to increase linearly with the mole fraction of oxygen in nitrogen. Over this range (0 to 41% O₂) the scission number increased from 1.5 to 5.0 and the polydispersity increased from 3.6 to 11.3 when the PMMA was degraded at the lower flux, while at the higher flux, the scission number increased from 5.0 to 14.4 with a concomitant polydispersity change from 2.0 to 4.5. These results show that gas phase O₂ reacts with the polymer chains, enhancing random scissions and generating functional groups from which depropagation is initiated. This enhanced decomposition increases the transient gasification rate leading to ignition and flame spread. Published by Elsevier Science Limited

1 INTRODUCTION

The thermal energy necessary for heat up and gasification of a bulk polymeric material has a major influence on the ignition and flame spread characteristics of that material. In fires, the mode of heat transfer predominantly takes the form of radiation and roughly resembles that from a blackbody at 1200 K.¹

The extent of influence of ambient oxygen on the transient gasification of a polymeric material receiving thermal radiation in a fire environment must be known in order to understand and correctly model this transient gasification process leading to ignition and flame spread. Virtually all current models of these aspects of material flammability ignore any possible role of gas phase oxygen in the gasification process (for example, see Ref. 1). However, in a study of the gasification rate of polymers degraded by

radiatively heating the surface of thermally thick samples, the rate of gasification and the surface temperature were found to be influenced significantly by the oxygen concentration in the surrounding atmosphere.² The effect of gas phase oxygen was more pronounced at an irradiance level of 17 kW/m² than a level of 40 kW/m². From the available experimental evidence it could be not determined whether the effect was due to chemical reactions or whether the gas phase oxygen was physically excluded from the surface by the increased evolution rate of decomposition products from the degrading surface.

The purpose of this study was to investigate, on a molecular level, the effect of atmospheric oxygen on the decomposition of poly(methyl methacrylate), PMMA. The approach was to measure the number of random chain scissions in the residual polymer after exposure of one

surface of a sample to thermally degrading radiation in a nitrogen atmosphere and other atmospheres containing various amounts of oxygen. By this approach we can determine the extent and depth within the bulk polymer that gas phase oxygen is involved in randomly introducing or enhancing scissions in the polymer chain. Each such scission results in one depolymerization site on one end of the scissioned chains and thus an enhanced gasification.

Previous studies^{3,5} have shown that the decomposition of PMMA in vacuum or an inert atmosphere, where the polymer had been prepared by a free radical mechanism, is initiated at two different temperatures. The temperatures correspond to two different energies of activation. PMMA prepared by an anionic mechanism shows only the higher activation energy for initiation of decomposition. The higher activation energy and higher decomposition temperature is attributed to initiation at random sites along the polymer chains. The initiation at the lower temperature was shown to originate at terminal vinyl groups which are weak links in the polymer chains. The vinyl group itself is the result of a hydrogen atom transfer between two macromolecular radicals undergoing termination reactions during free radical polymerization. A third site for decomposition of PMMA prepared by the free radical mechanism was demonstrated by Kashiwagi *et al.*⁶ at an even lower temperature, possibly originating at another weak link, sterically hindered head-to-head groups, which may arise from combination reactions of free radical ends of two growing chains.

During decomposition of PMMA, the monomer is assumed to arise from the polymer chain by a free radical mechanism, simply by reversing the polymerization reaction. Kashiwagi *et al.*⁷ demonstrated that other processes initiate depolymerization in the presence of oxygen, such that thermal initiation by random scission, at head-to-head groups, and at vinylidene chain ends no longer are the controlling factors for depolymerization. In the presence of oxygen a unique decomposition temperature is observed which is less than that for random scission in vacuum but greater than the vinyl-end-group initiation temperature.

We report the results of molecular weight measurements of PMMA thermally degraded in nitrogen containing from 0 to 41% oxygen and of

measurement of the residual monomer content in those samples. We also show the depth to which oxygen affects the degradation of the surface of PMMA. The extent of decomposition is calculated and expressed as a chain scission number. The monomer content in the residual polymer is expressed in terms of volume-to-weight per cent of methyl methacrylate (MMA) in PMMA

2 EXPERIMENTAL

2.1 Materials

The PMMA specimens used in this study were taken from commercial sheets nominally 13 mm (0.5 in) thick which were manufactured by Rohm and Haas Inc. and designated Plexiglas G.⁸ This material is indicated to contain about 0.1% of a parting agent, 0.5–0.7% of MMA, and a small quantity of an ultraviolet stabilizer. Sample squares were cut about 4 cm on a side for exposure to the thermal irradiance.

2.2 Radiative thermal decomposition

The apparatus used for decomposition of the PMMA by radiative heating in atmospheres with pre-selected oxygen concentrations has been illustrated and described elsewhere.² The heat source in this experimental apparatus is a 10 cm × 13 cm graphite plate, electrically heated by a well-regulated power supply. Gray body emission from the graphite plate is spectrally similar to the radiation from the flames of a developing compartment fire. The radiation from the heated plate is transmitted through a 9 cm × 9 cm water-cooled light pipe towards the sample, mounted vertically in a chamber. The exit of the light pipe is sealed with an NaCl window. The desired ambient atmosphere is fed from the bottom of the sample chamber at a controlled rate through a porous plate.

Decomposition of the PMMA samples was carried out at two flux levels, 17 and 30 kW/m². At each flux experiments were performed in a nitrogen atmosphere and in nitrogen containing 10.5, 20.8, and 41.3% oxygen for pre-selected periods of time. The samples were rapidly cooled by holding them over a liquid nitrogen bath after exposure to the irradiance.

2.3 Monomer content and molecular weight determination

Specimens 0.127 mm (0.005 in) thick were machined from the irradiated surface of the sample and at successive depths where gasification was evidenced by bubble formation. The machining was accomplished with a milling bit about 19 mm (0.75 in) in diameter. A portion of the PMMA cuttings was dissolved in tetrahydrofuran (THF) to make a 0.3% (g/ml of PMMA in THF) solution, generally about 5 ml. About one half of the solution was set aside in a screw-cap vial for the gas chromatography (GC) measurement of residual monomer. The remainder of the solution was further diluted with THF to bring the solution concentration down to 0.10% (g/ml). This solution was reserved for the size exclusion chromatography (SEC) determination of molecular weight and polydispersity of the polymer residues.

The GC measurements of residual monomer were made using a Hewlett Packard model 5890 instrument fitted with a 30 m \times 0.25 mm Supelco-wax coated capillary column. The column was maintained at 70°C. The injection port was held at 115°C and the flame ionization detector was operated at 300°C. The carrier gas through the system was helium. The detector response was calibrated with solutions of MMA in THF at known concentrations. Solution volumes ranging from 1 to 3 μ l were injected.

The characterization of the PMMA with respect to its molecular weight and molecular weight distribution was made by SEC using a Waters Associates Model ALC/GPC-150C gel permeation chromatograph. The instrument was equipped with a set of five Microstyrogel packed columns having pore sizes of 10^{-1} , 10^0 , 10^1 , 10^2 , and 10^{-2} μ m (10^3 , 10^4 , 10^5 , 10^6 , and 100 Å), respectively. The columns were calibrated with molecular weight standards of polystyrene and PMMA over a molecular weight range from about 500 to 3.8×10^6 g/mol.

3 RESULTS AND DISCUSSION

3.1 Monomer concentration in irradiated PMMA surfaces

The monomer content at various depths within the irradiated surface was measured in order to

determine if a concentration gradient of the monomer exists within the degrading polymer melt. A concentration gradient gradually increasing with distance from the surface would indicate that the decomposition product, MMA, could not readily escape as depropagation occurs. Conversely, no significant gradient in the monomer concentration within the irradiated surface would indicate that the monomer vaporized as it was formed. The monomer solubility in the degraded polymer will then control the concentration of residual monomer in the degraded surface.

Monomer concentrations at several depths from the exposed surface of the PMMA are plotted in Figs 1 and 2 for samples irradiated, respectively, at 17 and 30 kW/m². We estimate that the repeatability of this measurement is determined by the uncertainty of inserting one to three microliters of the solutions into the chromatograph. The standard uncertainty is estimated to be about $\pm 20\%$.

Samples degraded at the lower flux in the presence of O₂ tend to have the higher concentrations of MMA nearest to the exposed surface. The higher concentration apparently is the result of gas phase O₂ enhancing the generation rate of MMA, the primary decomposition product. It may be seen that the O₂ effect is limited to a depth of about 1 mm or less. This is the depth of openings in the exposed PMMA surface formed when trapped bubbles of MMA vapor burst and escape the melt. On the other hand, the uppermost surface layer of

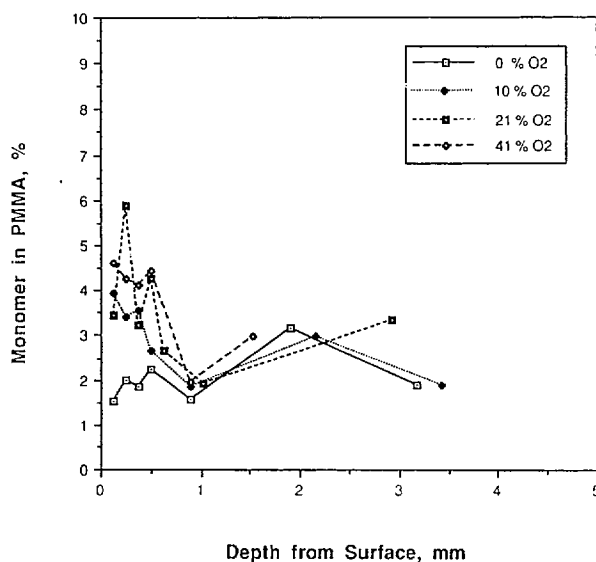


Fig. 1. Monomer content in PMMA after radiatively heating the surface for 420 s at 17 kW/m².

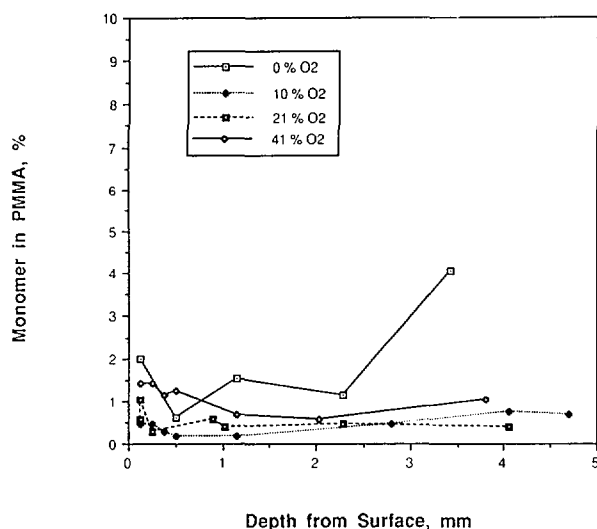


Fig. 2. Monomer content in PMMA after radiatively heating the surface for 420 s at 30 kW/m².

PMMA samples irradiated in N₂ at 17 kW/m² contained the lowest concentration of MMA within relatively small concentration gradient in the first millimeter of the exposed sample surface. Since the opposite effect was observed in atmospheres containing O₂, this supports the postulate that O₂ is significantly involved in the process of generating MMA at 17 kW/m².

Figure 2 shows the results of PMMA samples which were irradiated at 30 kW/m² in N₂ and in the presence of O₂. In this plot there are smaller differences between the MMA content at the surfaces and at various depths below the surface than between those of the samples irradiated at 17 kW/m². This indicates that the unzipping of the polymer to monomer and its subsequent vaporization are, for the most part, thermally controlled at the irradiance of 30 kW/m². At this incidence thermal flux depropagation and vaporization of the monomer may be influenced only slightly by the gas phase oxygen.

The effect of gas phase oxygen on the monomer content in the degrading PMMA melt appears to be most prominent near the exposed surface. The effect of oxygen on the concentration of MMA retained in the surfaces of PMMA irradiated at 17 and 30 kW/m² is illustrated in Fig. 3 by plotting only the amount of MMA retained in the surface layer (0.1 mm thick) against the oxygen mole fraction of the atmospheres in which the PMMA surfaces were irradiated. Although the monomer content appears to be affected by the presence of oxygen there is not an apparent dependence on the oxygen mole fraction. Here we see, however, that

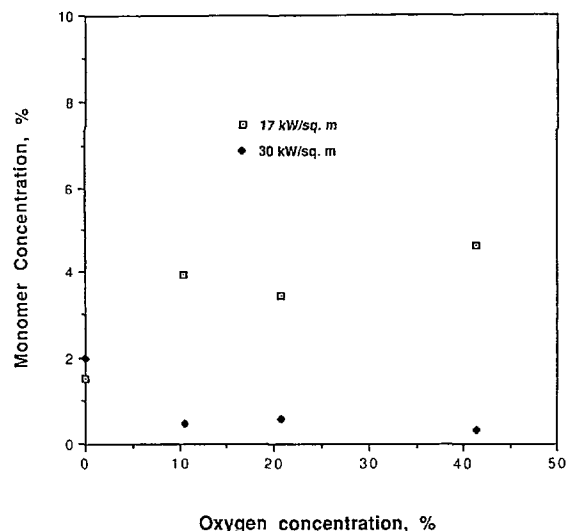


Fig. 3. Dependence of monomer content at the surface layer on oxygen concentration and external flux.

the concentrations of MMA in the surface layers are significantly greater in the surfaces irradiated in the presence of oxygen at the lower flux, 17 kW/m². Additionally, the monomer concentration is similar when oxygen is present. Where oxygen is not present, that is in nitrogen, the monomer concentration is essentially the same for each flux. The surfaces irradiated at 30 kW/m² in the presence of O₂ contain considerably less monomer as a result of more evaporation from these surfaces at higher temperatures and a less viscous melt generated by the higher incident thermal flux.

3.2 Gas phase oxygen effect on molecular weight and polydispersity

Figure 4 shows plots of the number average molecular weight (M_n) of PMMA at various distances from the surface of samples irradiated at 17 kW/m² for 420 s. There are four plots derived from experiments performed in atmospheres containing 0, 10, 21, and 41% oxygen in nitrogen. The lines connecting the points for each set are meant only to facilitate illustrating which values are from the same experiment in the respective atmospheres. Within the set of M_n values from a given atmosphere containing oxygen, the lowest values are found near the surface. The M_n values increase sharply down to about 0.5 mm below the surface. This depth suggests the extent to which oxygen has penetrated. The penetration depth (well beyond a plausible diffusion depth) is attributed to openings

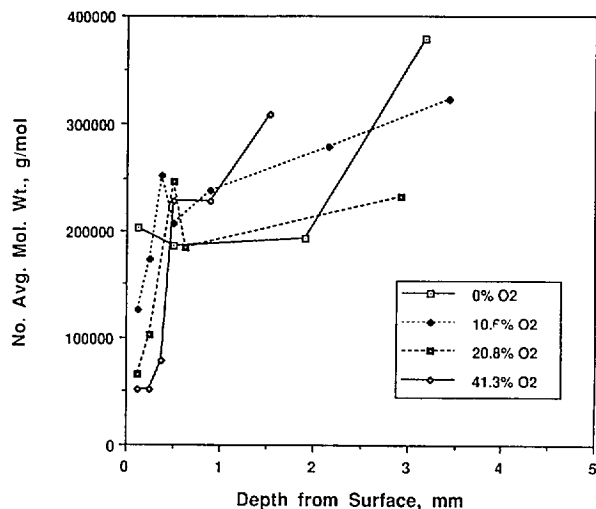


Fig. 4. Molecular weight versus distance to the surface of PMMA irradiated for 420 s at 17 kW/m².

created in the surface as a result of bubbles of MMA vapor bursting into the atmosphere from within the sample where thermal depolymerization has occurred. Beyond the O₂ penetration depth M_n continues to rise as one passes through a zone of purely thermal decomposition.

We know from previous work² that a slightly lower surface temperature is observed for PMMA irradiated at 17 kW/m² in 41% oxygen (in nitrogen) than the surface temperature of PMMA irradiated at the same flux in 100% nitrogen. The lower temperature of the surface is attributed to increased cooling caused by a greater gasification rate and a decreased activation energy as a result of an enhanced rate of

decomposition in the presence of oxygen. The higher temperature (as much as 30°C) in pure nitrogen is perhaps not surprising now, in view of differences in the M_n values at the surface; these certainly suggest a chemical role for oxygen in lowering M_n .

Next we look at the effect of atmospheric oxygen on the polydispersity, M_w/M_n , of the residual PMMA, where M_w is the weight average molecular weight. Figure 5 shows these results for PMMA irradiatively heated at 17 kW/m². Nearest the surface, the lower flux gives rise to broadening of the molecular weight distribution (MWD), as measured by the polydispersity, in the presence of oxygen and this broadening increases with oxygen concentration. In contrast there is minimal variation of MWD with distance from the surface degraded in the nitrogen atmosphere. In the oxygen-containing atmospheres the polydispersity variation seems to be small beyond a depth of about 0.5 mm and is probably not significant. These trends are further evidence of the active role oxygen has in the chain scission and depropagation of PMMA at lower thermal flux levels.

We now look at the results of irradiating the PMMA at a higher flux, 30 kW/m². Figure 6 shows plots of M_n at a number of levels within the irradiated surface. The samples in the plots were irradiated for 420 s in atmospheres containing 0, 10, 21, and 41% oxygen in nitrogen, as described above for the decomposition performed at the lower flux. The lowest molecular weight is seen again to be in the surface layer for

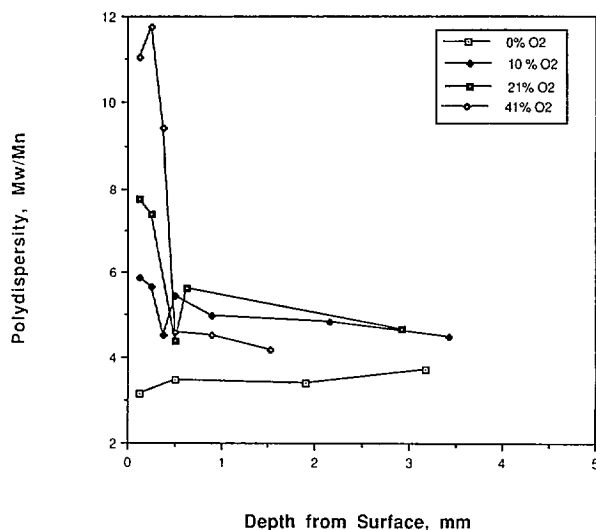


Fig. 5. Polydispersity of the surface of PMMA radiatively heated for 420 s at 17 kW/m².

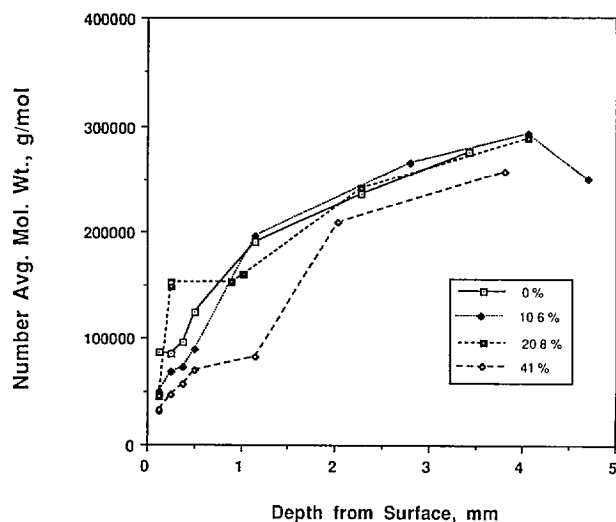


Fig. 6. Molecular weight versus distance to the surface of PMMA irradiated for 420 s at 30 kW/m².

each set of data plotted. Generally, the M_n values show an increase with distance from the surface and any influence of oxygen in depth is largely obscured by the noise in the data (except, perhaps, at 41% O_2). This suggests that the decomposition at the higher flux, 30 kW/m² in this case, is more nearly controlled by temperature alone. A substantially reduced dependence on ambient oxygen² at this flux is consistent with this inference.

Figure 7 shows the polydispersity with respect to depth for the decompositions at 30 kW/m². At this flux, the surface layers have the narrowest molecular weight distributions both in pure nitrogen and in the presence of oxygen. The values, with the exception of one unexplained value in the 41% O_2 seem to approach rather smoothly some asymptotic value at a depth of about 1.3 mm. We again infer from this observation that the decomposition at the higher flux is largely thermally controlled with oxygen participation being seen only at the highest O_2 concentration.

The effect of oxygen on the surface layers alone is shown in Fig. 8. The data are adequately represented by straight lines for samples degraded at 17 and 30 kW/m². The polydispersities at the lower flux show a much larger dependence on the oxygen mole fraction while the polydispersities at the higher flux are much less.

To show the degree of decomposition of the residual PMMA normalized in some conventional way, we plot the scission number of the

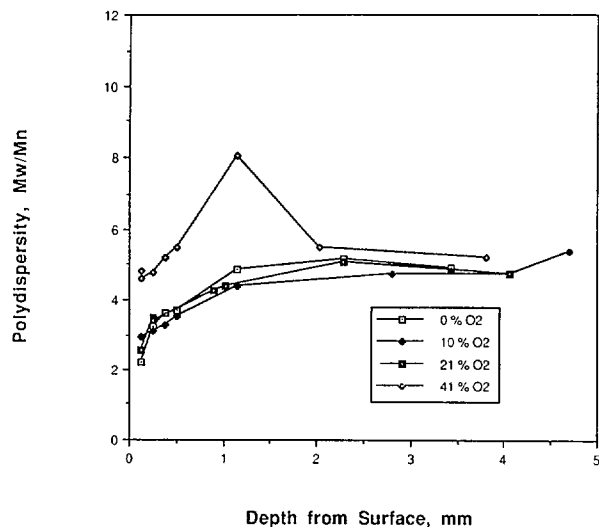


Fig. 7. The polydispersity of the surface of PMMA radiatively heated at 30 kW/m² for 420 s.

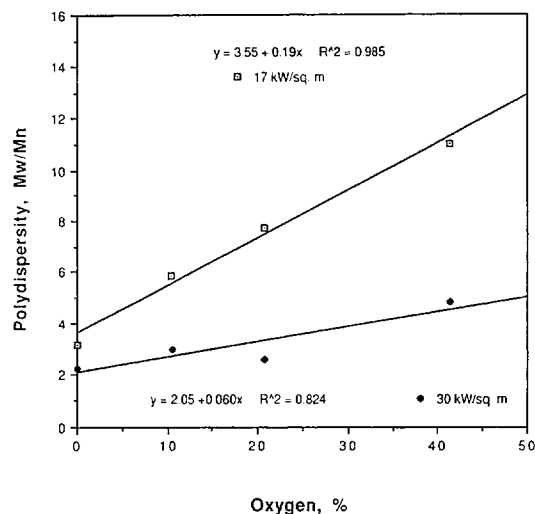


Fig. 8. Oxygen effect on the polydispersity of the residual surface layer.

polymer chains with respect to depth. We define the scission number as the number of times the original polymer chains are to be broken (scissioned) to achieve the observed molecular weight of the degraded polymer. The scission numbers may be expressed as follows:

$$S = \left\{ (M_n)_{\text{original}} / (M_n)_{\text{final}} - 1 \right\}$$

Figures 9 and 10 give the results obtained at 17 and 30 kW/m², respectively, in each of the atmospheres utilized. The trends shown in Figs 9 and 10 with regard to oxygen and flux effects are more clear here than in the plots of molecular weights previously shown in Figs 4 and 6. It is quite obvious here that the number of scissions

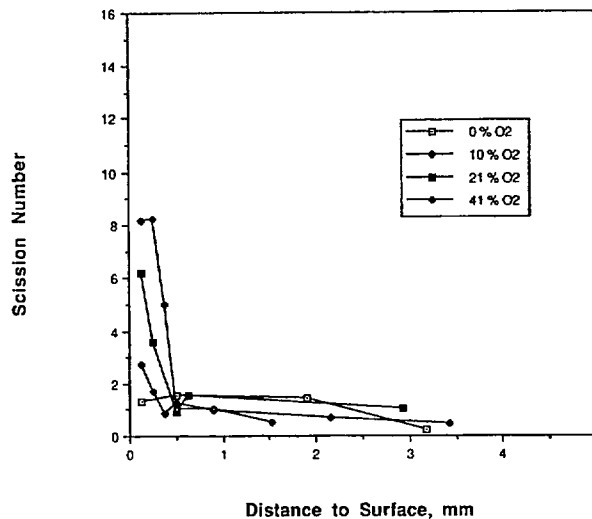


Fig. 9. Chain scission number of PMMA surfaces radiatively heated at 17 kW/m² for 420 s.

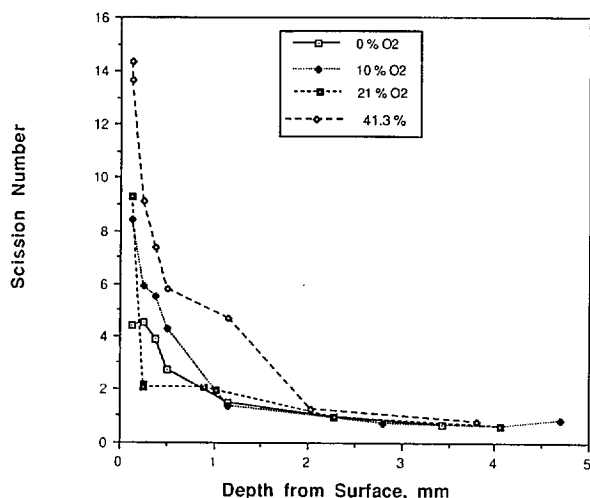


Fig. 10. Chain scissions near the surface of PMMA radiatively heated at 30 kW/m² for 420 s.

beyond the penetration depth of gaseous oxygen, about 0.5 mm at 17 kW/m² and about 1.3 mm (or less) at 30 kW/m², approaches an average value of about one or less. It can be seen that the scission numbers are greater at the higher flux. The scission numbers are a measure of both oxygen and heat effects in fragmenting the polymer chains. Fragmentation of the chain produces one chain end with a weak link capable of initiating depolymerization.

Figure 11 shows a linear dependence of scission number in the surface layer (0.13 mm thick) with respect to oxygen concentration in the surrounding atmosphere. It may be seen clearly that the number of chain scissions is oxygen concentration dependent at both the high and low flux. Moreover, the rates of change in the

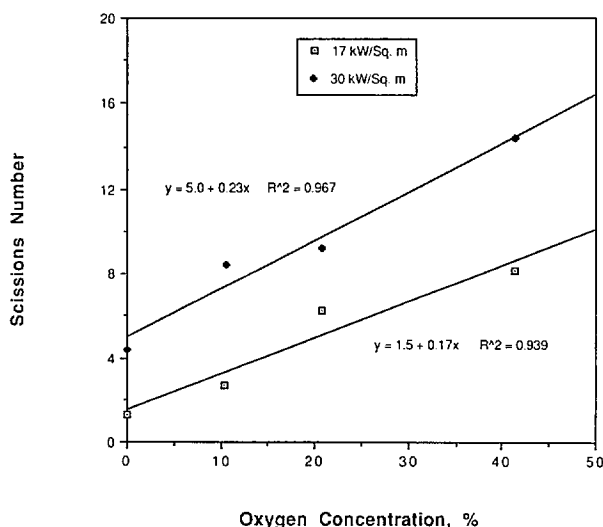
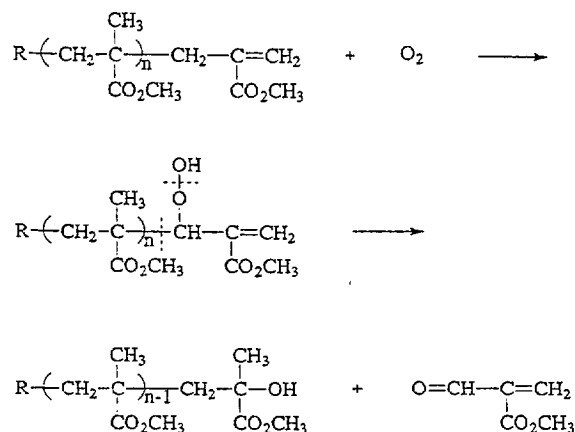


Fig. 11. Comparison of scission number dependence on oxygen concentration at two fluxes.

scission number with respect to oxygen mole fraction are quite similar for the decomposition at 17 and 30 kW/m² as seen by the respective slopes, 0.17 and 0.23 scissions/mol% O₂. An indication of the thermal effect may be seen by comparing the number of scissions in nitrogen at the two fluxes. In nitrogen atmospheres the scission number is about 1.5 at 17 kW/m², while it is about 5.0 at the irradiance of 30 kW/m². This represents an increase in scission number by a factor of 2.9 due solely to the thermal effect. For comparison we consider the number of scissions ascertained in room air (21 mol% O₂). The respective scission numbers are calculated to be 5.0 at the lower flux and 9.8 at the higher flux which represents an increase by a factor of 1.9 (94%). The scission number increases by a factor of 3.3 in going from 1.5 scissions in nitrogen to 5.0 scissions in 21% oxygen at the lower flux. This increase is slightly greater than the effect of the flux increasing from 17 to 30 kW/m². At the higher flux the scission number increases by a factor of about 2.0 in going from 5.0 in nitrogen to 9.8 in ambient air. These observations show that O₂ is significantly involved in the degradation reaction at both the high and low flux but to a greater extent at the lower flux.

We have previously shown^{6,7} that gas phase O₂ enhances gasification by initiating random chain scission but that it inhibits gasification initiated at weak links in the chains. A scheme by which gas phase oxygen might stabilize a weak link such as the terminal vinyl group is illustrated in Scheme 1. In this scheme oxygen can attack the most labile hydrogen activated by the terminal vinyl group, and to a small extent the ester groups, forming a hydroperoxide. The peroxide might thermally decompose by a beta-scission process



Scheme 1.

forming an hydroxyl ($-\text{OH}$) terminated polymer chain and a carbonyl ($-\text{C}=\text{O}$) vinyl ester compound. It should be noted that no test was made for this compound, an oxo-vinyl ester, nor has its identity been suggested by this investigation.

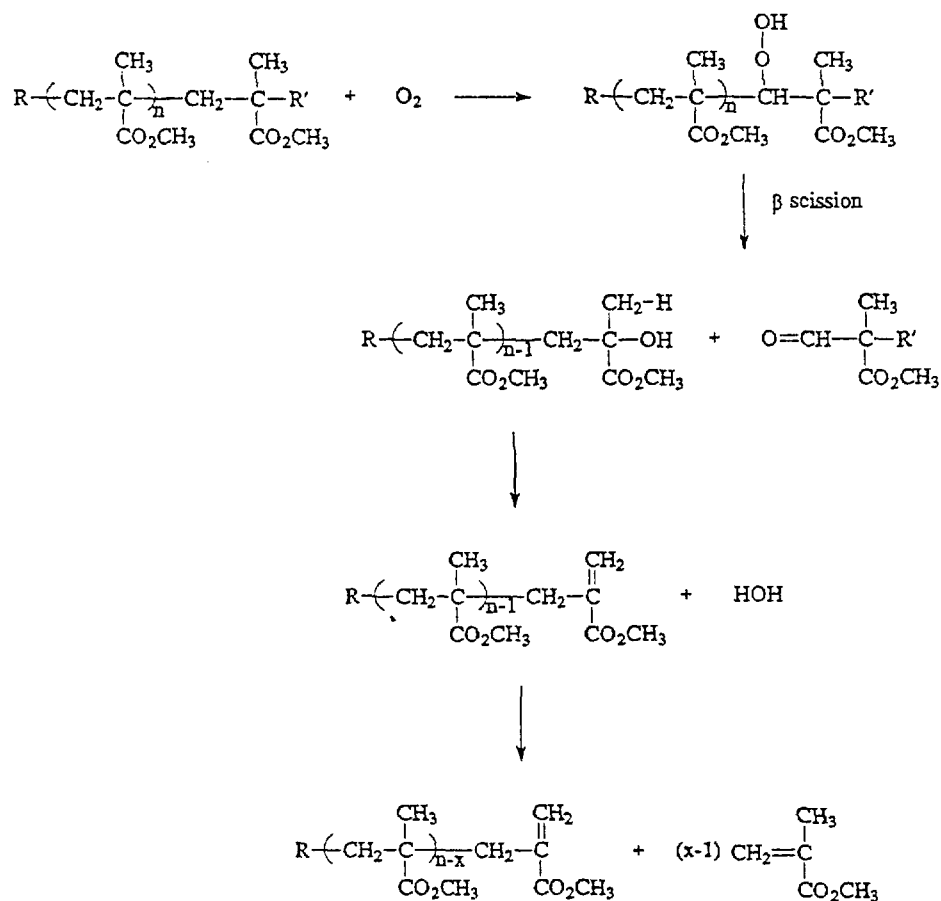
The hydroxyl-terminated macromolecule is expected to be more stable thermally than the vinylidene-terminated PMMA but not as stable as the backbone of PMMA from which random scissions are made at temperatures above 280°C . This postulation is suggested as a mechanism by which oxygen could stabilize and circumvent the weak-link initiated depropagation of PMMA.

Much earlier Koz'mina and Shirshova⁹ reported chain scission in PMMA in the presence of oxygen at 200°C without evolution of monomer. Chain scissions within the polymer chains were thought to occur at points where peroxide groups were formed by the reaction with molecular oxygen. Wall and Brown,¹⁰ a few years later, demonstrated that the decomposition of hydroperoxide groups formed by gamma-irradiation of PMMA in air was associated with

chain scissions. Thermal decomposition of a hydroperoxide on a PMMA chain should yield two molecules by beta-scission—one molecule with a terminal carbonyl group and the other with an alcohol group. Alcohols such as *tert*-butyl and *tert*-amyl, are believed to undergo a unimolecular decomposition, similar to that for alkyl halides, which would eliminate water and form the corresponding vinyl compound.¹¹ Barnard¹² determined the activation energy for this reaction as 228 kJ/mol (54.5 kcal/mol) which is considerably more than the activation energy of PMMA depropagation in air.^{7,13}

We thus suggest a simplified mechanism in Scheme 2 for the involvement of gas phase oxygen leading to a *tert*-hydroxy-terminated PMMA chain. This reaction is thought to occur below the depropagation reaction temperature of PMMA. Hence chain scission without depolymerization would result in an increase in M_w/M_n .

Thus it is proposed that the basic role of oxygen in the depolymerization of PMMA is simply to cause random chain scission and to



Scheme 2.

generate a weak link, a terminal vinyl functional group, from which depolymerization occurs. This enhanced decomposition must increase the transient gasification process since the surface temperature at 420 s has been shown² to be at or approaching a constant value and other investigations^{14,15} have established that the surface temperature of PMMA at pilot ignition is independent of external thermal flux.

Because one chain fragment of the chain scission process has a saturated end, it cannot participate in depolymerization from that end until a scission process by peroxide groups or proton transfer occurs. The results of this type of reaction are two-fold: (1) a lowering of molecular weight of the residual polymer, and (2) a broadening of the MWD. The first effect was seen from the scission number behavior in Fig. 11 and the broadening of the molecule weight distribution is shown in Fig. 8 in plots of polydispersity against oxygen concentration at the polymer surface.

In Fig. 8 the oxygen-dependency of the polydispersity of the surface layers at the lower and higher fluxes supports the idea suggested above. The flux at 30 kW/m² is sufficiently high to initiate depropagation from random thermal scission in the chains and the polydispersity varies little with ambient oxygen. Therefore this scission process is enhanced only slightly by the gas phase oxygen while at 17 kW/m² the polydispersity increase with ambient oxygen level is much greater. Obviously there is competition between purely thermally initiated chain scission and oxidatively initiated chain scission. Since the oxygen supply is limited to that which can diffuse in from the surrounding atmosphere, at the higher flux chain scission is shifted towards thermal initiated depropagation.

4 CONCLUSIONS

The monomer content of the surface layer is greater at the lower flux since the lower temperature at this condition causes a reduced gasification rate. At the higher flux, the generation and gasification of MMA is temperature controlled and is, to a lesser extent, affected by gas phase oxygen.

Gas phase oxygen significantly affects the decomposition of PMMA. This effect is confined, for the most part, to the near surface of the

polymer. The depth of O₂ reaction is limited to the depth of openings in the surface caused by bursting of bubbles of MMA vapor. The involvement of oxygen in the generation of monomer and in chain scission is more pronounced at an incident thermal flux of 17 kW/m² than at an incident flux of 30 kW/m². We conclude that chemical factors, oxidative reactions, increase the rate of gasification and, consequently, lower the surface temperature of bulk PMMA irradiatively heated in the presence of gas phase oxygen over that heated in nitrogen at the same irradiance. The scission number both at high and low thermal irradiances increases linearly with the mole fraction of atmospheric oxygen.

The role of gas phase oxygen in the decomposition mechanism of PMMA is proposed to be the generation of functional groups in the surface of the condensed phase (the PMMA melt) from which depropagation is initiated. We hypothesize that this functional group is an activated terminal vinylidene group. These new terminal vinylidene groups are proposed to arise from hydrogen atom transfer following thermally induced random scission and by an elimination reaction of a terminal hydroxyl and proton to form water and the vinyl-terminated macromolecule, PMMA. The hydroxyl groups arise from beta-scission of a proposed intermediate hydroperoxide formed on the backbone of the polymer chains. Since only one fragment of the beta-scissioned chain initiates depolymerization, the polydispersity of PMMA increases and the molecular weight decreases as the decomposition proceeds in the presence of molecular oxygen. These dependencies are oxygen concentration dependent.

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